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# Reaction Kinetics of $O(^3P)$ and OH With Diamine Rocket Fuels

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# REACTION KINETICS OF $O(^3P)$ AND OH WITH DIAMINE ROCKET FUELS

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## ABSTRACT

The gas phase kinetics of $O(^3P)$ and OH reactions with the three diamine fuels; $N_2H_4$, $CH_3NHNH_2$ and $(CH_3)_2NNH_2$ has been studied in a discharge flow-tube apparatus. The reactions were studied in 2 torr of He under pseudo-first-order conditions in the transient species concentration with a known excess of diamine concentration. The steady-state concentration temporal profiles of the transient species were directly monitored by fluorescence techniques to deduce the absolute second-order reaction rate coefficients. The Arrhenius expressions; $(7.35 \pm 2.16) \times 10^{-13} e^{(640 \pm 60)/T}$, $(2.71 \pm 0.04) \times 10^{-11} e^{-(190 \pm 50)/T}$ and $(1.96 \pm 0.29) \times 10^{-11} e^{(20 \pm 40)/T}$ $cm^3$ $molec^{-1}$ $s^{-1}$ in the temperature range 252-640 K were obtained for reactions of $O(^3P)$ with $N_2H_4$, $CH_3NHNH_2$ and $(CH_3)_2NNH_2$, respectively. The corresponding expressions; $(1.25 \pm 0.19) \times 10^{-11} e^{(315 \pm 55)/T}$, $(2.88 \pm 0.04) \times 10^{-11} e^{(210 \pm 55)/T}$ and $(2.00 \pm 0.30) \times 10^{-11} e^{(330 \pm 80)/T}$ $cm^3$ $molec^{-1}$ $s^{-1}$ in the range 232-374 K were determined for the OH reactions. Our recent measurement of the total yield of $OH(X^2\Pi)$ formation in the O + $N_2H_4$ reaction of $(0.15 \pm 0.05)$ at 298 K (of which ~ 50% was found to be produced hot with vibrational excitation up to the limit of reaction exothermicity) and the present observed experimental kinetic trends suggest that the initial addition of $O(^3P)$ and OH to the hydrazine molecule followed by rapid dissociation to products is an important process. Alkylation in the diamine molecule also allows direct H-abstraction mechanism to operate in these reaction systems.

## INTRODUCTION

The reactions of atomic oxygen ($O(^3P)$) and the hydroxyl radical (OH) with diamine fuels like hydrazine ($N_2H_4$), mono methyl hydrazine ($CH_3NHNH_2$) and unsymmetrical dimethyl hydrazine ($(CH_3)_2NNH_2$) are important elementary processes during combustion in bi-propellant (diamine/nitrogen tetroxide ($N_2O_4$)) rocket motors such as those in the Titan launch vehicles. Also, numerous spacecraft that operate in low earth orbit (LEO), ~ 180 km and above, use $N_2H_4$ in attitude-control jets and its mono-methylated analogue as a fuel in thruster engines such as those on the Space Shuttle. Although most of the fuel is consumed in the rocket chamber, some escapes in the unburned state especially at engine shut down. Since the ambient atmosphere at LEO altitudes consists mainly of atomic oxygen, the ejected fuel fragments are thought to degrade primarily via the $O(^3P)$ reaction. Even though molecular band emissions in the uv (and visible) have been observed in O-atom/diamine rocket plumes and flames,[1-5] the understanding of the chemical pathways involved is far from complete. Competition between pyrolysis and initial oxidation of the fuel needs to be understood to establish the mixing ratio of the exhaust effluents. The products of these processes themselves undergo further oxidation reactions of which some may directly produce the excited state species in chemiluminescent reactions, or produce metastable precursors. These precursors can then transfer their electronic energy to the surrounding ground state species. The quantum yields for uv/visible radiation from these excited species will depend on their radiative and reactive lifetimes. The latter being determined by both physical quenching and chemical transformations. One also needs to consider the possible effect of the relative velocity between the

exhaust fragments and the ambient O-atoms for any given oxidation reaction considered. The relative velocity can range from the sum of the LEO velocity (typically ~ 7.8 km $s^{-1}$) and the exhaust plume velocity (typically ~ 3.5 km $s^{-1}$) to the difference in the two values depending on the direction of the rocket firing. The role of ionized chemical species and of $O_2$ in the plume/thermosphere must also be investigated. Only when the interplay between the various processes described above is properly understood can we hope to make reliable predictions/assessments of uv/visible-plume signatures, and other spacecraft-plume effects such as the Shuttle Glow, and the contamination of spacecraft surfaces or onboard instrumentation.

Since the initial thermospheric oxidation reactions of the exhaust effluents will determine the way in which the subsequent plume chemistry unfolds, we have chosen in this work to investigate and properly characterize the reaction chemistry of the diamine fuel plus O-atom interactions under laboratory conditions. In the very near future, we shall report on the O-atom and $O_2$ oxidation chemistry of several different pyrolyzed fuel fragments found in diamine exhaust plumes.

Also, hydrazine fuels can be released into the lower atmosphere as a result of inadvertent spills of propellants or due to a launch abort. Monitoring the atmospheric concentrations of these species both in the gas phase and in aerosols, and modeling their transport and chemical transformations are essential to the evaluation of their environmental human health impact and launch constraint scenarios. The two main tropospheric oxidants for these fuels are expected to be OH and $O_3$. Here we also report the gas phase kinetics of OH reactions.

## EXPERIMENTAL TECHNIQUE

The discharge flow-tube apparatus employed in this work has previous been described in detail elsewhere.[6] A schematic of the apparatus is shown in Fig. 1. Here we only provide details of the experimental procedures employed to determine the reaction rate coefficient data. A small sample of liquid diamine was vaporized using He and carried into an absorption cell for 213.9-nm photometric determination of its gas phase concentration before sending the mixture for further dilution via a sliding injector into the flow-tube carrying an excess flow of He. The uv-absorption cross sections of $\sigma_{213.9}$ = 220.5 x $10^{-20}$, 248.9 x $10^{-20}$ and 399.9 x $10^{-20}$ $cm^2$ $molec^{-1}$, respectively for $N_2H_4$, $CH_3NHNH_2$ and $(CH_3)_2NNH_2$ were used.[7,8] A fixed side-arm microwave discharge port was used to introduce the $O(^3P)$ or OH into flow-tube. $O(^3P)$ was made either from the discharge of a 1% mixture of $O_2$ in He or pure $N_2$. In the latter case, the N-atoms produced were titrated in a flow of 1% mixture of nitric oxide in He. The titration reaction, N + NO $\rightarrow$ O + $N_2$, was followed to the end-point photometrically by monitoring the $NO_2^*$ emission produced in the accompanying reaction, O + NO $\rightarrow$ $NO_2^*$. OH was made from the discharge of a 1% mixture of $H_2$ in He to produce H-atoms, followed by the quantitative titration, H + $NO_2$ $\rightarrow$ OH + NO, or from the discharge of a 1% mixture of $CF_4$ in He to make F-atoms, followed by the reaction, F + $H_2O$ $\rightarrow$ OH + HF. The number density of the diamine in the reaction zone of the flow-tube was always in an excess of the initial radical number density, by 50-1000 times, and calculated from the known flow rates used to carry out the dilution, and the measured pressure and temperature of the reaction zone and the absorption cell. The capacitance manometers, the chromel-alumel thermocouples and the electronic mass flow meters used to flow the gases had previously been calibrated.

The reaction zone temperature in the experiments was varied in the range 232-640 K and the flow-tube operated at a pressure of 2 torr of He (a few experiments were done at 8 torr). Typical linear gas velocity, v, of 1800-3500 cm $s^{-1}$ of He flow was maintained in the 1-inch-diameter flow-tube. The plug-flow conditions[9,10] thus established in the flow-tube allowed us to follow the reaction kinetics of the [radical] in a known excess of [diamine] under pseudo-first-order conditions. Typical initial radical concentration was in the range (1-5) x $10^{10}$ molec $cm^{-3}$. The steady-state [radical] was monitored as a function of the reaction distance, z, between the point of reagent mixing at the injector tip and the fixed detection zone downstream of the flow-tube. The $O(^3P)$ was excited at 130.2-130.6 nm using a microwave discharge lamp and monitored orthogonally to it by cw-resonance fluorescence detection using photon-counting techniques.[6,11,12] The OH was probed using a tunable pulsed laser operating at ~ 282.15 nm to excite the $Q_12$ line of the OH transition, ($A^2\Sigma^+$, v' = 1 $\leftarrow$ $X^2\Pi$, v" = 0). The resulting laser-induced fluorescence due to the transitions, ($A^2\Sigma^+$, v' = 1 $\rightarrow$ $X^2\Pi$, v" = 1, bandhead at 312.16 nm) and ($A^2\Sigma^+$,

v' = 0 → $X^2\Pi$, v" = 0, bandhead at 306.36 nm), ensuing from the detection zone was detected orthogonally to the laser beam by gated-charge integration/signal averaging techniques.[6,13] The inner walls of the flow-tube were suitably coated to minimize radical loss rates at the surfaces. Most of the O-atom work was carried out in a resistively heated quartz flow-tube that had been cleaned in a 30% $H_3PO_4$ solution, while all OH (and some O-atom) work was done in a halocarbon coated Pyrex flow-tube with an outer Pyrex heating jacket. No systematic dependence of the measured reaction rate coefficient was observed on switching the movable diamine inlet to a fixed side-arm inlet and the fixed radical inlet to a suitable sliding source.

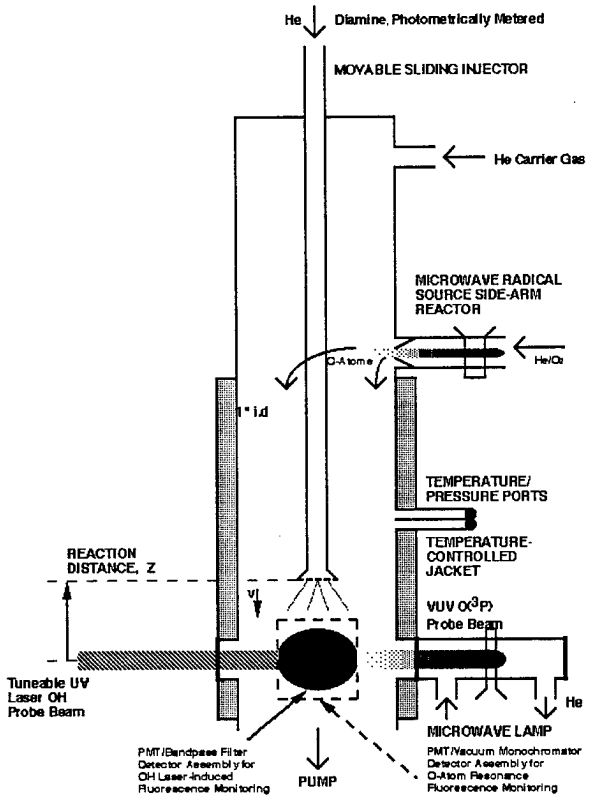


FIG. 1. Schematic of one version of the discharge flow-tube apparatus employed in this work.

## Materials

He (>99.9997%) carrier gas from U. S. Bureau of Mines and $N_2$ (99.9995%) from Spectra Gases were used as received. Hydrocarbon-free $N_2H_4$ (Viking Grade) from Edwards AFB, $(CH_3)_2NNH_2$ (>99.3%) and $CH_3NHNH_2$ (>99.5%) from Olin Chemicals were subjected to several freeze-thaw purification cycles at a grease-less vacuum line, and the purified distillates dried over BaO or $CaH_2$. NO (99.0%) supplied by Matheson Gas Products was passed slowly through a trap containing silica gel at 173 K to remove most of the $NO_2$ and $N_2O$ impurities and then frozen in a second trap over silica gel maintained at 77 K. The condensate was subjected to thorough pumping. NO was taken out from this trap as it warmed up slightly above 77 K and transferred into a 12-ℓ Pyrex bulb where it was diluted with He to make up a standard 1% NO in He titration mixture. $NO_2$ (99.9%) from M. G. Scientific Gases was mixed with excess $O_2$ to react away any NO present and the mixture collected in a trap over silica gel at 213 K. The excess $O_2$ and any other volatiles were pumped off and the condensate subjected to several freeze-thaw purification cycles. A standard 1% $NO_2$ in He titration mixture was prepared. $O_2$ (99.991%) from Big Three Industries, $CF_4$ (99.7%) from Scott Specialty Gases and $H_2$ (99.999%) from Linde Specialty Gases were used as supplied to make up 1% mixtures in He. The water was distilled in the laboratory.

## RESULTS

Since the [diamine] is always in a great excess over the [OH] in the flow-tube, it can be shown that the observed pseudo-first-order decay coefficient, k, for OH is given by, $\ln\{^{OH}S/^{OH}S_0\} = -k.t$. Where $^{OH}S$ is the net (background-subtracted) OH laser-induced fluorescence signal strength recorded at the detection zone for a reaction time of t = z/v. The flow-tube reaction distance, z, is defined to be the length between the tip of the injector where the diamine enters and the OH fluorescence detection axis. v is the bulk linear flow velocity of the He carrier gas. $^{OH}S_0$ is the signal strength that would be observed for z = 0 and corresponds to the initial concentration, $[OH]_0$, available at the detection zone when OH is introduced from the fixed side-arm reactor upstream of the flow-tube. (Note that a constant fraction of OH is lost to the flow-tube walls from the point where it enters and the point where it is detected. This loss term rate, $k_{W,OH}$, does not affect the above kinetic analysis, however, we have minimized it by coating the tube walls with thin films as described earlier, so as to maximize the observed signal-to-noise ratio. A similar analysis can be written for the $O(^3P)$ reactant.

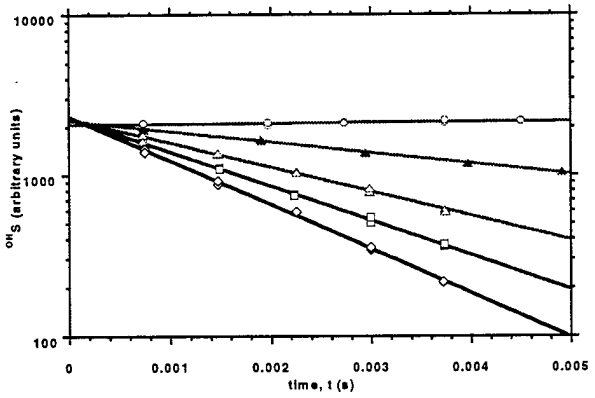


FIG. 2. Measured temporal profiles of OH signal, $OH_S$, in different $[(CH_3)_2NNH_2]$ = 0 (open circles), = 0.292 x $10^{13}$ (solid triangles), = 0.643 x $10^{13}$ (open triangles), = 0.957 x $10^{13}$ (open squares), and = 1.339 x $10^{13}$ molec $cm^{-3}$ (open diamonds) at 373 K and in 2 torr He.

Fig. 2 shows typical plots of the determined $OH_S$ signal on a logarithmic scale as a function of reaction time, t. The data points are the mean OH signals observed by averaging 100 fluorescence pulses. (Note that the time axis need not be absolute provided we accurately know the relative time increments (i.e. $\Delta z$) between the data points. The precision of z measurements is known to be very high (to within ± 0.05 cm) in our experiments.) The solid lines are exponential fits to the data points whose slopes yield values for the observed pseudo-first-order decay coefficients, k. The positive slope (open circles) obtained in the absence of $(CH_3)_2NNH_2$ is consistent with the loss of OH on the injector walls. As the injector is pulled back, less of its wall is exposed to the radical flow, and the OH signal increases. Typically this loss term, $k_{in}$, was measured to be ~ 10-20 $s^{-1}$, and was used to correct k to arrive at the net loss rate decay coefficient, $k_{net}$. Correction of $k_{net}$ for axial diffusion[9,10] using, $k_{corr} = k_{net}(1 + k_{net}\mathcal{D}/v^2)$, where $\mathcal{D}$, in units of $cm^2$ $s^{-1}$, is the diffusion coefficient of OH in He, resulted in ≤ 5.5% upward correction to the $k_{net}$ values.[14] The absolute second-order rate coefficient for the reaction, OH + $(CH_3)_2NNH_2$ → products, was determined from the slope of a plot of $k_{corr}$ versus $[(CH_3)_2NNH_2]$ employed. Fig. 3 shows a typical plot at 373 K with the linear-least-squares fit to the data points. Fig. 4 shows the observed temperature dependencies of the absolute second-order rate coefficients for the OH reactions with the three diamines studied here. The corresponding temperature dependencies of the $O(^3P)$ reactions are shown in Fig. 5.

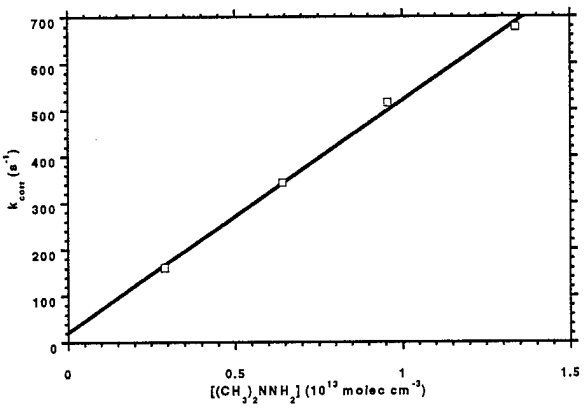


FIG. 3. Plot of corrected pseudo-first-order decay coefficients, $k_{corr}$, versus the $[(CH_3)_2NNH_2]$ of Fig. 2. The absolute second-order rate coefficient is (4.98 ± 0.75) x $10^{-11}$ $cm^3$ $molec^{-1}$ $s^{-1}$ at 373 K.

## DISCUSSION

### OH Reactions

The reactions of OH with the diamines are very fast, close to the gas-kinetic limit, and show slight negative temperature dependencies. The Arrhenius fits to the data points of Fig. 4 give the following expressions; (1.25 ± 0.19) x $10^{-11}$ $e^{(315 \pm 55)/T}$, (2.88 ± 0.04) x $10^{-11}$ $e^{(210 \pm 55)/T}$ and (2.00 ± 0.30) x $10^{-11}$ $e^{(330 \pm 80)/T}$ $cm^3$ $molec^{-1}$ $s^{-1}$, in the temperature range 232-374 K, for reactions with $N_2H_4$, $CH_3NHNH_2$ and $(CH_3)_2NNH_2$, respectively. Also, there is generally an increase in the OH reactivity along the above homologous series. Previous flash photolysis-resonance fluorescence study of Harris et al.[15] reported a weaker temperature dependence of 4.4 x $10^{-11}$ $e^{(116 \pm 176)/T}$ $cm^3$ $molec^{-1}$ $s^{-1}$, in the range 298-424 K, for the OH + $N_2H_4$ reaction. No dependence was observed on the Ar pressure which was varied in the range 25-50 torr. Also under these conditions, a temperature independent rate coefficient

of (6.5 ± 1.3) x $10^{-11}$ $cm^3$ $molec^{-1}$ $s^{-1}$ was reported for the OH + $CH_3NHNH_2$ reaction. However, for the OH + $(CH_3)_2NNH_2$ reaction, they could only estimate a room temperature value of (5 ± 2) x $10^{-11}$ $cm^3$ $molec^{-1}$ $s^{-1}$ because of severe handling problems encountered with this dialkylated diamine. At 298 K, Harris et al.'s values are ~ 80% larger, ~ 11% larger and ~ 17% smaller than our values for $N_2H_4$, $CH_3NHNH_2$ and $(CH_3)_2NNH_2$, respectively. An earlier communication from Hack et al.[16] for the OH + $N_2H_4$ reaction studied by discharge flow-tube-ESR technique reported a value of 2.2 x $10^{-11}$ $cm^3$ $molec^{-1}$ $s^{-1}$ at 298 K which is ~ 39% smaller than our value.

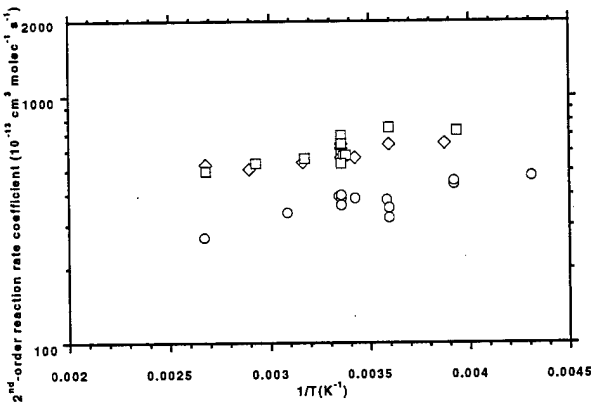


FIG. 4. The temperature dependencies of the absolute second-order rate coefficients for OH reactions with, $N_2H_4$ (open circles), $CH_3NHNH_2$ (open diamonds), and $(CH_3)_2NNH_2$ (open squares).

The lack of proper quantification of the diamine number density in the previous studies might possibly be one of the reasons as to why there is disagreement in the absolute values of some of the rate coefficients. We have made accurate, to within ± ~ 6%,[7] in-situ measurements of the [diamine] in our experiments and have confirmed that the measured rate coefficients are independent of the $[OH]_o$ range employed. The overall accuracy of the rate coefficients in this work is expected to be in the range ± (15-18)% (precision plus systematic errors included).[6] Some problematic wall effects were noticed when using $(CH_3)_2NNH_2$, especially at temperatures below 253 K. The flow-tube became easily contaminated with yellow oily deposits on prolonged exposures which resulted in unusually large OH wall loss rates compared to that observed in a freshly coated flow-tube with the halocarbon wax. This was evident from the larger than normal intercepts in $k_{corr}$ versus $[(CH_3)_2NNH_2]$ plots even at the lowest $[OH]_o$ used. The flow-tube was frequently re-waxed to minimize this problem. Data above 374 K could not be obtained in this flow-tube because of fogging of the optical windows due to condensation of the wax vapor which resulted in a dramatic fall in the signal-to-noise ratio of the fluorescence signal. The quartz flow-tube showed enhanced wall loss rates of OH in the presence of the diamine and was therefore not used. We shall report on the rate coefficients at temperatures, T > 374 K in the near future using a resistively heated pulsed photolysis reactor.[17]

The magnitude and the weak temperature and lack of pressure effects of the OH + $N_2H_4$ reaction rate coefficient suggests that the simple direct metathesis of H-atom may not be important compared to addition of the OH followed by dissociation of the intermediate into products. The findings of a recent ab initio study by Armstrong et al.[18] on this reaction are qualitatively consistent with the present experimental observations. The shape of the potential energy profile along the reaction coordinate leading to $N_2H_3$ + $H_2O$ as the products was examined. At the B3LYP/6-31+G(D, P) level, a single pre-reaction complex was found characterized by an OH--NN hydrogen bond (OH--N distance 1.859Å, H--N-N angle 170.1°). The G2(MP2) energy of this was lower by ~ 5.5 kcal $mol^{-1}$ than that of ($N_2H_4$ + OH). Also, MP2 optimization with the same basis set yielded essentially the same structure for the complex. However, no transition-state for the direct H-abstraction by OH could he located at the B3LYP/6-31+G(D, P) level. Any approach by OH to an endo-H of hydrazine resulted in H-atom loss without activation. Instead, a transition-state structure for inversion of the N-atom bearing a hydrogen in close proximity to the hydroxyl was located at this level (N-H--OH angle 120.7°, NH--OH distance 1.707 Å). The normal mode with the imaginary frequency suggested that N-inversion would be accompanied by H-atom loss since the separation between the H and O was decreased, while the N-H distance remained the same. The G2(MP2) energy of this transition-state was ~ 2.7 kcal $mol^{-1}$ above that of the separated reactants. By contrast, at MP2/6-31+G(D, P) level, a well defined transition-state structure for H abstraction by OH was found. This transition-state was directly connected to the hydrogen-bonded pre-reaction complex, with the G2(MP2) energy being ~ 1.3 kcal $mol^{-1}$ lower than that

of the reactants. Also, single-point QCISD(T)/6-31+G(D, P) calculations along the MP2 intrinsic reaction coordinate further confirmed the existence of an early transition-state well above the initial pre-reaction complex but below the separated reactants (the NN-H bond being broken was elongated by only ~ 7% while the H-OH bond forming had already reached a length that was ~ 1.5 times that of the final separation in the water molecule). Such a description of the energetics of the reaction intermediaries would predict a negative experimental activation energy and a pressure insensitive rate coefficient.[19] It would be most interesting to see how the computed barrier to H-abstraction and vibrational frequency information on the transition-state and pre-reaction complex predict the absolute magnitude and temperature dependence of the OH + $N_2H_4$ reaction rate coefficient by means of transition-state theory rate expressions.

The introduction of the $CH_3$ moiety in the hydrazine molecule opens up the possibility of direct H-abstraction from the stronger C-H bonds, or enhancement of hydrogen bonding tendency and eventual removal of the H-atom from the weak N-H bond which weakens even further due to the electron-donating effect of the methyl group. On the other hand, fewer N-H sites (but more C-H sites) are present on increased methylation. Experimentally, we see an increase in the measured rate coefficient for $CH_3NHNH_2$ and much less thereafter for $(CH_3)_2NNH_2$. Deuterium isotopic studies on the reaction rates and product yields will further help clarify the nature of the reaction mechanism in these systems.

Using an average [OH] of 5 x $10^6$ molec $cm^{-3}$ and a standard mean temperature of 279 K for the lower atmosphere, we calculate the lifetimes to be ~ 1.5, ~ 0.9 and ~ 0.9 hr, respectively for the oxidation of $N_2H_4$, $CH_3NHNH_2$ and $(CH_3)_2NNH_2$ by the hydroxyl radical. Ozone is also thought to react rapidly with these diamines.[20] However, the absolute rate coefficients for these reactions have not been measured. Proper atmospheric chemical lifetimes of these diamines will be calculable when this data becomes available.[17] This will allow reliable assessments to be made on the urban impact of the inherent toxicity and carcinogenic potency of the diamines (and their oxidation products such as dimethylnitrosamine from the $(CH_3)_2NNH_2$ + $O_3$ reaction) when they are accidentally released at vehicle launch pads or at fill stations.

**$O(^3P)$ Reactions**

Compared to OH, the $O(^3P)$ atom is less reactive towards the three diamines. However, the reactions are still fast and show weak temperature dependencies. The Arrhenius fits to the data points of Fig. 5 give the absolute second-order rate coefficient expressions; (7.35 ± 2.16) x $10^{-13}$ $e^{(640 \pm 60)/T}$, (2.71 ± 0.04) x $10^{-11}$ $e^{-(190 \pm 50)/T}$ and (1.96 ± 0.29) x $10^{-11}$ $e^{(20 \pm 40)/T}$ $cm^3$ $molec^{-1}$ $s^{-1}$, in the temperature range 252-640 K and in 2 torr of He, for reactions with $N_2H_4$, $CH_3NHNH_2$ and $(CH_3)_2NNH_2$, respectively. Again, an increase in the rate coefficient is observed along the indicated homologous series. For O + $N_2H_4$, Gehring and co-workers[21] reported much larger rate coefficients with a positive temperature dependence of 1.4 x $10^{-10}$ $e^{(-604/T)}$ $cm^3$ $molec^{-1}$ $s^{-1}$, in the temperature range 243-463 K and in 2.7 torr of Ar pressure. They used an excess of $[O(^3P)]$ and mass-spectrometrically monitored $[N_2H_4]$ decays in their discharge flow-tube system. Incorrect calibration of the $[O(^3P]$ and the presence of other much more reactive species could result in apparently enhanced $[N_2H_4]$ decays with a positive temperature dependence for the measured rate coefficient. Lang[22] used a photolytic method to produce O-atoms in an excess of [diamine] and monitored the $[O(^3P)]$ decay by cw-resonance fluorescence in 1-50 torr of $N_2$ pressure. No pressure dependence of the rate coefficient was seen. The values at 296 K are higher than our measured values by ~ 55%, ~ 12%, and ~ 10%, respectively for $N_2H_4$, $CH_3NHNH_2$ and $(CH_3)_2NNH_2$. The presence of unknown reactive impurities in Lang's sample of $N_2H_4$ would result in an apparently larger second-order rate coefficient. In light of the good agreement for the values of $CH_3NHNH_2$ and $(CH_3)_2NNH_2$, this problem doesn't seem to be significant in the alkylated samples.

Checks were performed to show that our measured rate coefficients were independent of the He pressure (up to 8 torr) or the $[O(^3P)]_0$ range employed ((0.1-20) x $10^{11}$ molec $cm^{-3}$). Above ~ 640 K, slight charring in the quartz flow-tube was seen, indicating that thermal decomposition of the alkylated diamines was occurring. Below ~ 252 K, the waxed flow-tube required frequent cleaning to remove the oily deposits from prolonged exposure to the diamine flow. Thus rate data beyond these temperature limits was not collected.

In our previous work,[6] we showed that the O + $N_2H_4$ reaction proceeded ~ 15% of the time via single-H-abstraction to give OH as the product (~ 50% of which is produced vibrationally hot). Other earlier work has shown that the preferred reaction channel is the elimination of $H_2O$ in a direct reaction via a cyclic-transition-state involving the HN-NH system.[21,23] As the OH can form from 4 similar N-H sites and the $H_2O$ only from 2 distinct HN-NH approaches, the per site O-atom rate coefficient for OH and $H_2O$ production in $N_2H_4$ is calculated to be 2.36 x $10^{-13}$ and 26.8 x $10^{-13}$ $cm^3$ $s^{-1}$, respectively. Since the $H_2O$ formation channel should not be possible in $(CH_3)_2NNH_2$, and assuming no change in the N-H bond reactivity, the per $CH_3$ group rate coefficient for (the only remaining) H-abstraction channel by the O-atom is then calculated to be 103 x $10^{-13}$ $cm^3$ $s^{-1}$. This would then predict a total $CH_3NHNH_2$ rate coefficient of 135 x $10^{-13}$ $cm^3$ $molec^{-1}$ $s^{-1}$, which compares well with our value of 143 x $10^{-13}$ $cm^3$ $molec^{-1}$ $s^{-1}$ of Fig. 5. Also, if the assumptions of the reaction mechanism we have made are correct we should observe an OH yield of close to unity in the O + $(CH_3)_2NNH_2$ reaction and ~ 80% in the corresponding $CH_3NHNH_2$ reaction. These OH yield measurements are currently in progress. Excitation of OH vibrations in these reactions has also been seen.[17]

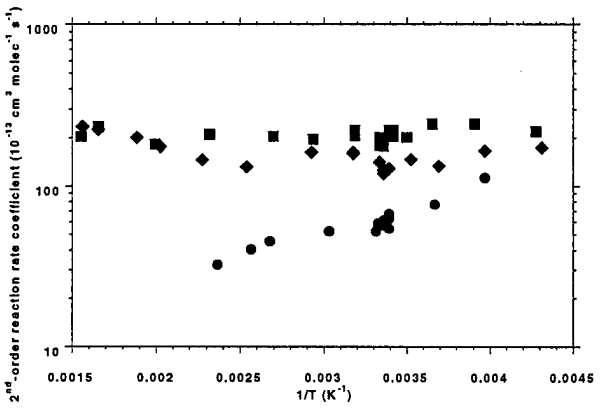


FIG. 5. The temperature dependencies of the absolute second-order rate coefficients for $O(^3P)$ reactions with, $N_2H_4$ (solid circles), $CH_3NHNH_2$ (solid diamonds), and $(CH_3)_2NNH_2$ (solid squares).

However, the good agreement between the observed rate coefficients and the above analysis might just be fortuitous, since there is some evidence in the literature that the N-H bond strength might be varying in the alkylated diamines.[23-26] We might then expect a trend in the reaction rate at the N-H sites as well as at the C-H sites of the methyl moiety, where reactivity of the C-H bond might also vary depending on the degree of methylation at the N-center. Precise conclusions as to which of the two effects is more important can not yet be drawn. Studies using D-substituted diamine analogs where kinetic isotope effects are measured, and product identities and absolute branching yields are determined should help clarify the situation.

It is encouraging to know that in the related amine homologous series: $NH_3$, $NH_2CH_3$, $NH(CH_3)_2$ and $N(CH_3)_3$, a similar trend for reaction with O-atoms is observed.[27,28] The 298 K reaction rate coefficient increases with increasing methylation, indicating perhaps increased importance of reaction at the C-H site. Though, it must also be noted that both the N-H and C-H bond strengths decrease with increased methylation in this amine series.[29] For OH reactions, the reactivity trend is: $NH_3$ < $NH_2CH_3$ < $N(CH_3)_3$ < $NH(CH_3)_2$, thus showing here, that where possible, the N-H site competes with the C-H site.[27,30] Since in reality, both the pre-exponential factor and the activation energy for a given reaction channel determine the overall reaction probability, only when product yields are measured can we say which reaction path is the preferred mode for H-abstraction. Such measurements have been performed for H-atom, O-atom and OH radical reactions with alkanes. For the series: $CH_4$, $CH_3CH_3$, $(CH_3)_2CH_2$ and $(CH_3)_3CH$, the total observed rate coefficients increase from left to right for all three reactants.[27,31-33] It has further been shown that for $(CH_3)_2CH_2$ and $(CH_3)_3CH$, there is preferential removal of the secondary and tertiary hydrogens by the three transient species. The secondary and tertiary C-H bonds in these molecules are known to be weaker than the C-H bonds on the methyl moiety. Hence in these reactions there is a strong correlation between the bond strength and the observed reaction rate at the bond site of interest.

The negative temperature dependence and the lack of a pressure dependence we observe for $O(^3P)$ + $N_2H_4$ reaction is not inconsistent with a mechanism involving the formation of an adduct as was the case for the corresponding OH reaction. Subsequent

decomposition of this, in principle, may lead to a variety of products;

$O(^3P) + N_2H_4 \rightarrow [N_2H_4O]^* \rightarrow$

| | $\Delta H_{298K}$(kcal mol$^{-1}$) |
|---|---|
| $H_2NOH + NH$ | (-1.4) |
| $H_2NO + NH_2$ | (-20.5) |
| $HNO + NH_3$ | (-69.6) |
| $OH + N_2H_3$ | (-26.3) |
| $H_2O + N_2H_2$ | (-90.2) |

We have already assessed the importance of the forth channel to be minor by direct laser-induced fluorescence detection of the OH.[6] Currently we are in the process of quantifying NH, $NH_2$ and HNO by this technique also.[17] Previous mass-spectrometric ion-current yield measurements[21,23] at m/e of 31 for $N_2H_3$ (or HNO), at 30 for $N_2H_2$, at 18 for $H_2O$, and at 17 for OH (or $NH_3$) qualitatively confirm our OH observations, and suggest channel five to be the dominate process. Direct ir-observations of $N_2H_2$ are desirable to confirm this.[17] Also, ab initio studies on the energy and geometrical profiles of possible reaction intermediates and transition-states for this reaction would help in the proper elucidation of the nature of the reaction mechanism.

Assuming an average $[O(^3P)]$ of 1 x $10^{12}$ molec cm$^{-3}$ at LEO altitudes, the estimated thermospheric lifetimes are ~ 0.6 s, ~ 47 ms, and ~ 78 ms, respectively for $N_2H_4$, $CH_3NHNH_2$ and $(CH_3)_2NNH_2$ at a typical temperature of 800 K. Chemical lifetimes in the immediate vicinity of the spacecraft exhaust may be even shorter because of higher $O(^3P)$ concentrations and due to reactions with other effluents. By analogy, we might expect the $N_2H_2$ molecule to also react rapidly with the $O(^3P)$, preferentially via the removal of two H-atoms to give $(N_2(A) + H_2O)$ as the main products. The subsequent energy transfer reactions of the metastable nitrogen, $N_2(A)$, would then provide a mechanism to produce electronically excited radicals such as $OH(A^2\Sigma^+)$, $NH(A^3\Pi)$, $NH_2(\tilde{A}^2A_1)$, and $NO(A^2\Sigma^+)$ which have previously been observed in rocket plume environments. The yield of $N_2H_2$ in channel 5 and from the subsequent oxidation of $N_2H_3$ from channel 4 will govern the maximum uv-radiance one can expect from the above scheme. To understand the relative importance of uv-excitation by this method compared to that from other sources of $N_2(A)$, or due to alternate precursor energy transfer reactions like those of CO(a), or that resulting from direct chemiluminescent reactions involving carbonaceous species, a detailed knowledge of the chemical and physical composition of the alkylated diamine rocket plumes will be required.

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